



King's Research Portal

DOI:

[10.1364/OE.27.008180](https://doi.org/10.1364/OE.27.008180)

Document Version

Publisher's PDF, also known as Version of record

[Link to publication record in King's Research Portal](#)

Citation for published version (APA):

Zhou, N., Wang, P., Shi, Z. X., Gao, Y. X., Yang, Y. X., Wang, Y. P., ... Tong, L. M. (2019). Au nanorod-coupled microfiber optical humidity sensors. *OPTICS EXPRESS*, 27(6), 8180-8185. [356169].
<https://doi.org/10.1364/OE.27.008180>

Citing this paper

Please note that where the full-text provided on King's Research Portal is the Author Accepted Manuscript or Post-Print version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version for pagination, volume/issue, and date of publication details. And where the final published version is provided on the Research Portal, if citing you are again advised to check the publisher's website for any subsequent corrections.

General rights

Copyright and moral rights for the publications made accessible in the Research Portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognize and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the Research Portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the Research Portal

Take down policy

If you believe that this document breaches copyright please contact librarypure@kcl.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



Au nanorod-coupled microfiber optical humidity sensors

N. ZHOU,¹ P. WANG,² Z. X. SHI,¹ Y. X. GAO,¹ Y. X. YANG,¹ Y. P. WANG,³
Y. XIE,¹ D. W. CAI,¹ X. GUO,¹ L. ZHANG,¹ J. R. QIU,¹ AND L. M. TONG^{1,*}

¹State Key Laboratory of Modern Optical Instrumentation, College of Optical Science and Engineering, Zhejiang University, Hangzhou 310027, China

²Department of Physics and London Centre for Nanotechnology, King's College London, Strand, London WC2R 2LS, UK

³Department of Electrical and Computer Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA

*phytong@zju.edu.cn

Abstract: We demonstrate a high-sensitivity relative humidity (RH) sensor taking advantage of single-band narrow plasmon resonance of a single Au nanorod coupled to a whispering gallery cavity mode of a polyacrylamide microfiber. From the resonance peak shift, the sensor could achieve a sensitivity up to 0.51 nm/% RH with a cavity size of about 2 μm . By coupling multiple Au nanorods along the microfiber axis, we demonstrate a position-dependent microfiber optical humidity sensor with a 1.5-mm spatial resolution, which can be potentially reduced to micrometer level, paving a way toward high-resolution distributed microfiber optical sensors.

© 2019 Optical Society of America under the terms of the OSA Open Access Publishing Agreement

1. Introduction

Monitoring and controlling of relative humidity (RH) is crucial in diverse fields from electronics industry, corrosion protection, to disease diagnosis, among which humidity sensors with high sensitivity, fast response, low cost and compact size are highly desired. Compared to conventional electronic sensors, fiber-optic humidity sensors have special advantages including fast response, high bandwidth and immunity to electromagnetic interference [1–4]. For higher compactness and sensitivity, in past years, optical microfibers with diameter close to wavelength of the probing light have attracted extraordinary interest for optical sensing, and a number of miniature optical humidity sensors have been developed with various microfiber-based structures [1,4–6], in which the microfiber resonator is one of the mostly studied structures due to their high sensitivity and simple structures [7].

Typical microfiber resonators, in forms of assembled loops [8–10], tied knots [11–13], or stacked multicoils [14,15], are ring-type resonators. The ring size of this kind of resonators, from hundreds of micrometers to several millimeters, is limited by the bending loss of the microfiber, preventing the further miniaturization of the microresonator for higher compactness and spatial resolution (typically $> 40 \mu\text{m}$ in cavity size) [9–12,16–21].

Recently, it is found that, a plasmonic Au nanorod (NR) deposited on the surface of a microfiber can excite whispering gallery modes (WGMs) in the cross-section of the microfiber with diameter $< 10 \mu\text{m}$, and generate narrow-band localized surface plasmon resonance (LSPR) via strong coupling between the WGM and the LSPR modes [22], offering an opportunity for microfiber-based light-matter interaction on a smaller scale [23,24].

Here, by replacing the silica microfiber used in previous work [22–24] with a moisture-sensitive polyacrylamide (PAM) microfiber, we obtained single-band 10-nm-linewidth plasmon resonance from the coupled WGM and LSPR modes of the hybrid structure, with a cavity size of about 2 μm . Relying on the RH-sensitive resonance shift, we demonstrated an optical humidity sensor with high sensitivity within a large dynamic range. Then, by

depositing multiple Au NRs onto the microfiber to generate a series of distributed micrometer-scale hybrid cavities along the fiber axis, we demonstrated a prototype of distributed optical microfiber sensor with spatial resolution of 1.5 mm, which can be potentially reduced to the same level of the cavity size (i.e., $\sim 2\ \mu\text{m}$).

2. Experiments

PAM microfibers were fabricated by direct drawing of a 2 wt% PAM (molecular weight: 5,000,000 to 6,000,000; Acros Organics) aqueous solution. Because PAM microfiber is water-soluble, in our experiment, Au NRs in aqueous solutions (NanoSeedz Ltd.) were firstly adhered onto a silica fiber taper, then Au NRs were transferred to the surface of the PAM microfiber by micromanipulation. Briefly, a fiber taper was firstly immersed into a dilute Au NRs aqueous solution for a few seconds and dried in the open air for ~ 2 hours, with Au NRs adhered onto the surface of the fiber taper. Then, under an optical microscope, the fiber taper was mounted on a triple-axis micromanipulator was finely controlled to touch the surface of the PAM microfiber at an intersection angle of about 60° for several times, until single Au NRs were transferred onto the right position on the surface of the PAM microfiber.

To test the humidity sensing performance, the hybrid Au NRs/PAM structure was placed in an airtight poly(methyl methacrylate) chamber and the humidity was controlled by varying the ratio of dry and humidified nitrogen. The RH was detected by a commercial electronic hygrometer (EH) with its probe placed in the chamber. The resolution of the EH is 0.1%RH.

Optical properties of the hybrid Au NRs/PAM structure were characterized using a dark-field setup, as depicted in Fig. 1. A beam of unpolarized white light (SC-5, Wuhan Yangtze Soton Laser Co., Ltd.) from standard optical fiber was used to illuminate PAM microfiber coupled Au NR at an oblique angle of about 30° with respect to the microfiber axis, and a $50\times$ objective was used to collect the scattered light, which was then redirected to a charge-coupled device camera (DS-Fi2, Nikon) and a spectrometer (Maya2000-Pro, Ocean Optics). Using a dark-field microscope with a polarizer for imaging, it's easy to identify the orientation of a single Au NR from its scattering intensity, which presents a maximum when the selected polarization is along its longitudinal direction.

The morphology and size distribution of Au NRs were characterized by a transmission electron microscope (TEM, Hitachi HT7700), and the hybrid Au NR/PAM microfiber structure was characterized by a scanning electron microscope (SEM, Zeiss Utral 55).

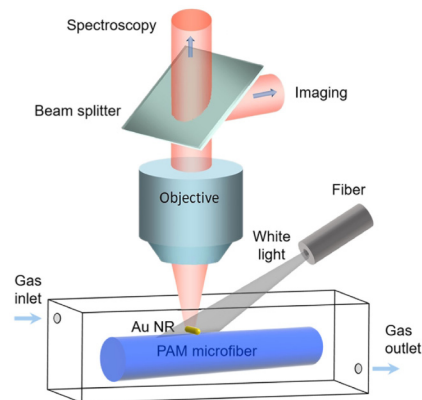


Fig. 1. Schematic illustration of the experimental setup for RH sensing.

3. Results and discussion

3.1. Single-cavity-based optical RH sensor

We used a side-illuminated dark-field spectroscopy to investigate optical properties of single Au NRs coupled to a PAM microfiber. Figure 2 shows the scattering spectra of a single Au NR before and after coupling to the PAM microfiber. Before coupling, the longitudinal LSPR peak of an Au NR with length and diameter of about 110 nm and 38 nm deposited on a glass slide is about 700 nm with a linewidth of 46.5 nm (Fig. 2(a)). After the Au NR was coupled to a 2.1- μm -diameter microfiber, the linewidth of the dominant LSPR peak reduced to 8.0 nm (Fig. 2(b)). Here the linewidth is larger than that of hybrid Au NR and silica microfiber structure [22,23] due to the relatively larger optical loss of the polymer microfiber and the deviation of the NR orientation from vertical direction with respect to the microfiber length.

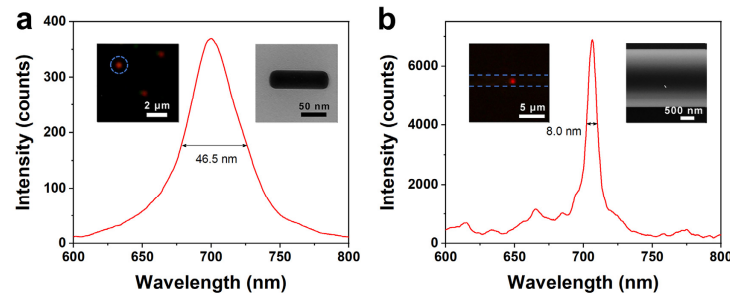


Fig. 2. Scattering spectra of a single Au NR before and after coupling to a PAM microfiber. (a) Scattering spectrum of an Au NR deposited on a glass slide. Top-left inset is the dark-field microscopy image (circled with a blue dotted line) and top-right inset is the transmission electron microscopy (TEM) image. (b) Scattering spectrum of an Au NR coupled to a PAM microfiber with diameter of 2.1 μm . Top-left inset is the dark-field microscopy image (the blue dotted lines outline the microfiber) and top-right inset is the corresponding SEM image.

Then the hybrid Au NR/PAM structure was placed in an airtight chamber with controllable humidity inside. When RH in the chamber is increased from 14.7 to 85.8%, the LSPR scattering spectra show a monotonous redshift as shown in Fig. 3(a). With RH increasing, more water molecules diffuse into the polymer microfiber, resulting in two competing factors: increased diameter of the microfiber (i.e., the WGM cavity) that leads to a redshift of the LSPR peak, and decreased refractive index of the microfiber that leads to a blueshift of the LSPR peak. Here the former factor overcompensates the later, resulting in a net redshift [10,25–27].

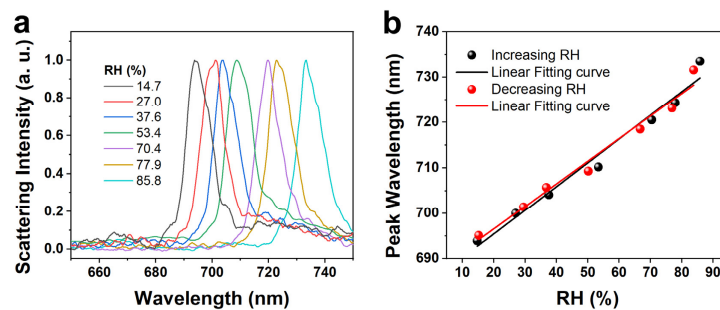


Fig. 3. Optical RH sensing based on a single hybrid cavity. (a) Normalized scattering spectra of the sensor with increasing RH. (b) Scattering peak wavelength as a function of RH with increasing (black dots) and decreasing (red dots) RH. The black and red lines are the linear fitting curves.

The dependence of the LSPR scattering peak wavelength on RH shows excellent linearity for both increasing and decreasing RH over a wide RH range (Fig. 3(b)), from which we obtain a sensitivity of about 0.51 nm/% RH. While this sensitivity is comparable with other high-sensitivity microfiber RH sensors [10,13,16,18–20,28–31], the hybrid nanorod-microfiber sensor is much more compact in size (i.e., the 2- μm cavity size of this sensor versus $> 40\text{-}\mu\text{m}$ cavity sizes of other sensors) [9–12,16–21]. The miniature cavity size is also beneficial to fast response, as has been shown in other types of microfiber optical sensors [10,25,32].

To estimate the detection resolution, we use a commonly accepted criterion that shifts of 1/100 of the linewidth can be detected with an adequate signal-to-noise ratio [31,33–35], and obtain the resolution of our sensor to be 0.16% RH, which is better than typical microfiber [9,31,36–39] or metallic nanoparticle [40,41] based humidity sensors.

3.2. Multiple-cavity-based distributed optical RH sensor

One special advantage of the hybrid nanorod-microfiber cavity is that, under appropriate illumination, wherever the nanorod deposited on the surface of the microfiber, it can locally excite a coupled LSPR and WGM mode. Since the coupled mode is confined within the micrometer-size cavity, when multiple nanorods are deposited along the fiber length, it is possible to generate a number of independent cavities for distributed optical sensing, as schematically illustrated in Fig. 4(a). To show this, we deposited three nanorods along a 2.1 μm -diameter microfiber, with 1.5 mm apart from each other. When a narrow stream of water vapor is blown onto the deposited area of the microfiber (Fig. 4(a)), a RH gradient along the microfiber length forms and the RH decreases successively from position P1 to P3, which is proved by the RH measurements using an EH (the open circles in Fig. 4(c)). LSPR scattering from the three nanorods, as shown in Fig. 4(b), gives different spectral shifts, clearly showing the RH gradient along the microfiber length, and confirming the possibility of developing distributed microfiber optical sensors with spatial resolution much higher than conventional fiber-optic sensors [42].

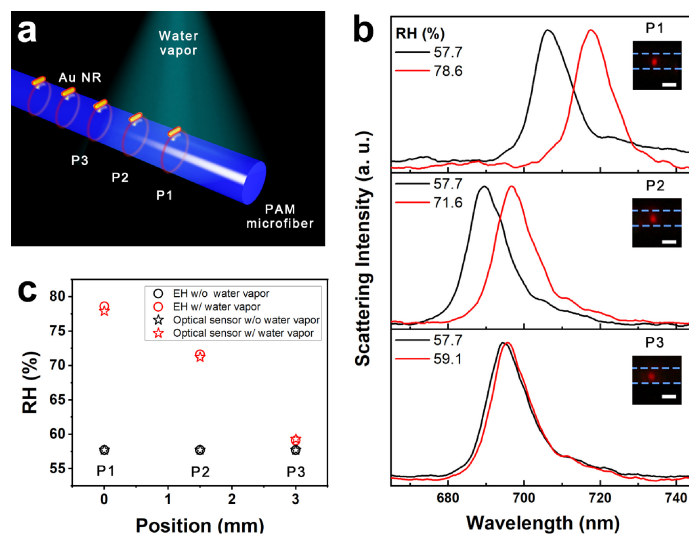


Fig. 4. Distributed optical RH sensing based on multiple hybrid cavities. (a) Schematic illustration of the experimental setup. (b) Normalized scattering spectra of 3 hybrid cavities at three different positions (denoted as P1, P2 and P3) before (RH = 57.7%) and after being exposed to water vapor. The insets are the corresponding dark-field microscopy images after being exposed to water vapor. The scale bars are 2 μm . (c) Position-dependent RH value measured by an electronic hygrometer (EH, circles) and this optical sensor (asterisks) before (black) and after (red) being exposed to water vapor, respectively.

It should be noted that, as shown in Fig. 4(c), the RH distribution measured by the hybrid-cavity optical sensor, which is obtained with the sensitivity from Fig. 3(b) (i.e., 0.51 nm/% RH), is in excellent agreement with that by the EH. Limited by the diameter of the sensing chip of the EH (~ 0.8 mm), the separation between Au NRs was chosen to be 1.5 mm here. Since the spatial resolution of the hybrid nanorod-microfiber sensor is only limited by crosstalk between neighboring cavities (which may happen with the separation down to the cavity-size scale, e.g., 2 μm) and the optical diffraction limit (less than 2 μm in this work) for distinguishing scattering signals from neighboring nanorods in spectral measurement, this kind of distributed fiber-optic sensors in principle can offer a spatial resolution on micrometer level.

4. Conclusions

In conclusion, based on coupled WGM and LSPR modes of a hybrid Au NR/PAM microfiber cavity, we have demonstrated an optical humidity sensor with high sensitivity, high detection resolution, high spatial resolution, small footprint and simple structure. Moreover, by producing multiple independent micrometer-size cavities along the same microfiber in a scalable way, we have also demonstrated a prototype of distributed optical microfiber sensor with high spatial resolution. The sensor configuration can be extended for sensing many other measurands when the PAM microfiber or Au nanorod is pre-functionalized or replaced with counterparts made of other materials [43,44]. Finally, the initial results shown here may pave a way towards a category of coupled nanoparticle-microfiber structures for compact, high sensitivity and distributed photonic and plasmonic sensing.

Funding

National Natural Science Foundation of China (61635009, 61475136, 11527901); Fundamental Research Funds for the Central Universities; China Postdoctoral Science Foundation (2017M621922).

References

1. L. Tong, "Micro/nanofibre optical sensors: challenges and prospects," *Sensors (Basel)* **18**(3), 903–929 (2018).
2. G. Y. Chen, D. G. Lancaster, and T. M. Monro, "Optical microfiber technology for current, temperature, acceleration, acoustic, humidity and ultraviolet light sensing," *Sensors (Basel)* **18**(2), 72–96 (2017).
3. S. Sikarwar and B. C. Yadav, "Opto-electronic humidity sensor: a review," *Sens. Actuators A Phys.* **233**, 54–70 (2015).
4. G. Brambilla, "Optical microfiber devices," *Opt. Laser Technol.* **78**, 76–80 (2016).
5. J. Lou, Y. Wang, and L. Tong, "Microfiber optical sensors: a review," *Sensors (Basel)* **14**(4), 5823–5844 (2014).
6. Y. Peng, Y. Zhao, M. Q. Chen, and F. Xia, "Research advances in microfiber humidity sensors," *Small* **14**(29), e1800524 (2018).
7. L. T. Gai, J. Li, and Y. Zhao, "Preparation and application of microfiber resonant ring sensors: a review," *Opt. Laser Technol.* **89**, 126–136 (2017).
8. M. Sumetsky, Y. Dulashko, J. M. Fini, A. Hale, and D. J. DiGiovanni, "The microfiber loop resonator: theory, experiment, and application," *J. Lightwave Technol.* **24**(1), 242–250 (2006).
9. N. Irawati, H. A. Rahman, H. Ahmad, and S. W. Harun, "A PMMA microfiber loop resonator based humidity sensor with ZnO nanorods coating," *Measurement* **99**, 128–133 (2017).
10. P. Wang, F. Gu, L. Zhang, and L. Tong, "Polymer microfiber rings for high-sensitivity optical humidity sensing," *Appl. Opt.* **50**(31), G7–G10 (2011).
11. J. C. Shin, M. S. Yoon, and Y. G. Han, "Relative humidity sensor based on an optical microfiber knot resonator with a polyvinyl alcohol overlay," *J. Lightwave Technol.* **34**(19), 4511–4515 (2016).
12. M. A. Gouveia, P. E. S. Pellegrini, J. S. Dos Santos, I. M. Raimundo, and C. M. B. Cordeiro, "Analysis of immersed silica optical microfiber knot resonator and its application as a moisture sensor," *Appl. Opt.* **53**(31), 7454–7461 (2014).
13. A. D. D. Le and Y. G. Han, "Relative humidity sensor based on a few-mode microfiber knot resonator by mitigating the group index difference of a few-mode microfiber," *J. Lightwave Technol.* **36**(4), 904–909 (2018).
14. F. Xu and G. Brambilla, "Demonstration of a refractometric sensor based on optical microfiber coil resonator," *Appl. Phys. Lett.* **92**(10), 101126 (2008).
15. Y. Yin, J. B. Yu, Y. X. Jiang, S. Li, J. Ren, G. Farrell, E. Lewis, and P. F. Wang, "Investigation of temperature dependence of microfiber coil resonators," *J. Lightwave Technol.* **36**(20), 4887–4893 (2018).

16. N. Irawati, T. N. R. Abdullah, H. A. Rahman, H. Ahmad, and S. W. Harun, "PMMA microfiber loop resonator for humidity sensor," *Sens. Actuators A Phys.* **260**, 112–116 (2017).
17. H. Ahmad, M. T. Rahman, S. N. A. Sakeh, M. Z. A. Razak, and M. Z. Zulkifli, "Humidity sensor based on microfiber resonator with reduced graphene oxide," *Optik (Stuttg.)* **127**(5), 3158–3161 (2016).
18. M. J. Faruki, M. Z. Ab Razak, S. R. Azzuhri, M. T. Rahman, M. R. K. Soltanian, G. Brambilla, B. M. Rahman, K. T. Grattan, R. De La Rue, and H. Ahmad, "Effect of titanium dioxide (TiO₂) nanoparticle coating on the detection performance of microfiber knot resonator sensors for relative humidity measurement," *Mater. Express* **6**(6), 501–508 (2016).
19. Y. Wu, T. H. Zhang, Y. J. Rao, and Y. Gong, "Miniature interferometric humidity sensors based on silica/polymer microfiber knot resonators," *Sens. Actuator B Chem.* **155**(1), 258–263 (2011).
20. Q. Tian, H. Z. Yang, Q. Z. Rong, Z. Y. Feng, R. H. Wang, M. K. A. B. Zaini, K. S. Lim, H. Ahmad, P. Zhang, X. Z. Ding, K. Lu, and Y. D. He, "Highly sensitive micro-hygrometer based on microfiber knot resonator," *Opt. Commun.* **431**, 88–92 (2019).
21. J. Shi, W. Xu, D. Xu, Y. Wang, C. Zhang, C. Yan, D. Yan, Y. He, L. Tang, W. Zhang, and J. Yao, "Humidity sensor based on intracavity sensing of fiber ring laser," *J. Phys. D Appl. Phys.* **50**(42), 425105 (2017).
22. P. Wang, Y. Wang, Z. Yang, X. Guo, X. Lin, X. C. Yu, Y. F. Xiao, W. Fang, L. Zhang, G. Lu, Q. Gong, and L. Tong, "Single-band 2-nm-line-width plasmon resonance in a strongly coupled Au nanorod," *Nano Lett.* **15**(11), 7581–7586 (2015).
23. Q. Ai, L. Gui, D. Paone, B. Metzger, M. Mayer, K. Weber, A. Fery, and H. Giessen, "Ultrannarrow second-harmonic resonances in hybrid plasmon-fiber cavities," *Nano Lett.* **18**(9), 5576–5582 (2018).
24. F. X. Gu, L. Zhang, Y. B. Zhu, and H. P. Zeng, "Free-space coupling of nanoantennas and whispering-gallery microcavities with narrowed linewidth and enhanced sensitivity," *Laser Photonics Rev.* **9**(6), 682–688 (2015).
25. F. Gu, L. Zhang, X. Yin, and L. Tong, "Polymer single-nanowire optical sensors," *Nano Lett.* **8**(9), 2757–2761 (2008).
26. R. A. Barry and P. Wiltzius, "Humidity-sensing inverse opal hydrogels," *Langmuir* **22**(3), 1369–1374 (2006).
27. F. Gu, H. Zeng, L. Tong, and S. Zhuang, "Metal single-nanowire plasmonic sensors," *Opt. Lett.* **38**(11), 1826–1828 (2013).
28. Y. Shao, Y. Wang, S. Cao, Y. Huang, L. Zhang, F. Zhang, C. Liao, and Y. Wang, "Mechanism and characteristics of humidity sensing with polyvinyl alcohol-coated fiber surface plasmon resonance sensor," *Sensors (Basel)* **18**(7), 2029–2037 (2018).
29. L. Bo, P. F. Wang, Y. Semenova, and G. Farrell, "Optical microfiber coupler based humidity sensor with a polyethylene oxide coating," *Microw. Opt. Technol. Lett.* **57**(2), 457–460 (2015).
30. L. P. Sun, J. Li, L. Jin, Y. Ran, and B. O. Guan, "High-birefringence microfiber sagnac interferometer based humidity sensor," *Sens. Actuator B Chem.* **231**, 696–700 (2016).
31. B. Gu, M. Yin, A. P. Zhang, J. Qian, and S. He, "Optical fiber relative humidity sensor based on FBG incorporated thin-core fiber modal interferometer," *Opt. Express* **19**(5), 4140–4146 (2011).
32. P. Wang, L. Zhang, Y. Xia, L. Tong, X. Xu, and Y. Ying, "Polymer nanofibers embedded with aligned gold nanorods: a new platform for plasmonic studies and optical sensing," *Nano Lett.* **12**(6), 3145–3150 (2012).
33. F. Vollmer and S. Arnold, "Whispering-gallery-mode biosensing: label-free detection down to single molecules," *Nat. Methods* **5**(7), 591–596 (2008).
34. L. Labrador-Páez, K. Soler-Carracedo, M. Hernández-Rodríguez, I. R. Martín, T. Carmon, and L. L. Martín, "Liquid whispering-gallery-mode resonator as a humidity sensor," *Opt. Express* **25**(2), 1165–1172 (2017).
35. A. Bozzola, S. Perotto, and F. De Angelis, "Hybrid plasmonic-photonic whispering gallery mode resonators for sensing: a critical review," *Analyst (Lond.)* **142**(6), 883–898 (2017).
36. M. Batumalay, S. W. Harun, N. Irawati, H. Ahmad, and H. Arof, "A study of relative humidity fiber-optic sensors," *IEEE Sens. J.* **15**(3), 1945–1950 (2015).
37. G. Y. Chen, X. Wu, Y. Q. Kang, L. Yu, T. M. Monro, D. G. Lancaster, X. Liu, and H. Xu, "Ultra-fast hygrometer based on U-shaped optical microfiber with nanoporous polyelectrolyte coating," *Sci. Rep.* **7**(1), 7943–7949 (2017).
38. Y. Luo, C. Chen, K. Xia, S. Peng, H. Guan, J. Tang, H. Lu, J. Yu, J. Zhang, Y. Xiao, and Z. Chen, "Tungsten disulfide (WS₂) based all-fiber-optic humidity sensor," *Opt. Express* **24**(8), 8956–8966 (2016).
39. N. Irawati, H. A. Rahman, M. Yasin, S. Al-Askari, B. A. Hamida, H. Ahmad, and S. W. Harun, "Relative humidity sensing using a PMMA doped agarose gel microfiber," *J. Lightwave Technol.* **35**(18), 3940–3944 (2017).
40. J. Qin, Y. H. Chen, B. Y. Ding, R. J. Blaikie, and M. Qiu, "Efficient plasmonic gas sensing based on cavity-coupled metallic nanoparticles," *J. Phys. Chem. C* **121**(44), 24740–24744 (2017).
41. A. W. Powell, D. M. Coles, R. A. Taylor, A. A. R. Watt, H. E. Assender, and J. M. Smith, "Plasmonic gas sensing using nanocube patch antennas," *Adv. Opt. Mater.* **4**(4), 634–642 (2016).
42. Z. Ding, C. Wang, K. Liu, J. Jiang, D. Yang, G. Pan, Z. Pu, and T. Liu, "Distributed optical fiber sensors based on optical frequency domain reflectometry: a review," *Sensors (Basel)* **18**(4), 1072–1102 (2018).
43. H. Chen, L. Shao, Q. Li, and J. Wang, "Gold nanorods and their plasmonic properties," *Chem. Soc. Rev.* **42**(7), 2679–2724 (2013).
44. H. Wei, D. Pan, S. Zhang, Z. Li, Q. Li, N. Liu, W. Wang, and H. Xu, "Plasmon waveguiding in nanowires," *Chem. Rev.* **118**(6), 2882–2926 (2018).